QUASI-DEGENERACY IN BOUND-STATE QED. FINE STRUCTURE OF HELIUMLIKE IONS

INGVAR LINDGREN, STEN SALOMONSON, BJÖRN ÅSÉN, and
ANN-MARIE MÅRTENSSON-PENDRILL
Department of Physics, Chalmers University of Technology and Göteborg University, SE 41296 Göteborg, Sweden

A new procedure for bound-state QED, based upon a covariant form of the time-evolution operator is reported. This procedure is applicable also to systems with closely spaced or *quasi-degenerate* levels, where the standard S-matrix formalism can generally not be used due to *quasi-singularities*. We have applied the procedure to the heliumlike ions of neon and argon, and produced the first numerical QED results for a complete fine-structure splitting. Good agreement is obtained with recent experimental data. The new procedure is closely related to standard many-body perturbation theory (MBPT), which may open up possibilities to combine QED and MBPT in a more systematic way.

1 Introduction

There is presently a renewed interest in the study of the fine structure of helium and heliumlike ions, the main reason being that accurate comparison of experimental and theoretical data can lead to an independent determination of the fine-structure constant α [1,2,3,4].

Quite recently a very accurate measurement of the fine-structure separation $2\,^3P_1 - 2\,^3P_0$ in neutral helium has been reported with an accuracy of 30 ppb [5]. Compared with accurate analytical calculations [4] this yields a value of the fine-structure constant, 1/137.0359864(31), which *differs from the accepted value by four standard deviations*. Quite accurate values exist also for the separations in heliumlike ions, some of which are shown in Table 1 [6,7,8,9,10,11].

The most accurate QED calculations on heliumlike ions are performed by means of the analytical $Z\alpha$ expansion, which works well for low Z. For higher Z the convergence rate decreases drastically, and a rapidly increasing number of terms is needed to reach high accuracy. For high Z, where $Z\alpha$ approaches unity, the power expansion cannot be used, and it is necessary to utilize numerical methods, using a Furry-like picture, which corresponds to an expansion to all orders in $Z\alpha$.

The standard numerical technique for bound-state QED is based upon the S-matrix formulation with the Gell-Mann–Low–Sucher procedure [12,13]. Such calculations have been performed for the *ground state* of heliumlike ions [14,15,16,17] and also to some excited states of such ions [18,19]. Generally, however, this technique is not applicable for excited states with multiplet structure, where the states can be very closely spaced or *quasi-degenerate*. Presently, only two procedures are available for dealing with such problems in its full generality, namely the *two-times Green's-function procedure*, developed by Shabaev and coworkers [20,21,22,23] and the *covariant evolution-operator procedure*, recently developed by us [24,25].

Table 1: Experimental data for some fine-structure separations of He-like ions in the $1s2p$ multiplet. (The values for Z=2 and 3 are in MHz, the remaining ones in cm^{-1})

Z	$^3P_1 - ^3P_0$	$^3P_2 - ^3P_0$	$^3P_2 - ^3P_1$	Expt'l method
2	29616.9509(9) [a]		2291.175(1) [b]	Laser spect.
3	155704.3(9) [c]		-62678.4(9) [c]	Laser spect.
7	8.6707(7) [d]			Laser spect.
9			957.8730(12) [e]	Laser spect.
10		1856(1) [f]		Solar flare
12	833.133(15) [g]	4404.6(2,1) [f]		Laser spect./Solar flare
18		27425(5) [h]		Beam foil

[a] George *et al.* [5] [b] Storry *et al.* [2], Castilla *et al.* [3] [c] Riis *et al.* [6] [d] Thompson *et al.* [7]
[e] Myers *et al.* [8] [f] Curdt *et al.* [9] [g] Myers *et al.* [10] [h] Kukla *et al.* [11]

Another approach to deal with the structure of heliumlike ions is to use many-body procedures of various kind, where the electron correlation can be treated essentially to all orders, and corrected for QED effects by using the analytical expansion. The shortcoming of such an approach is that it is difficult to go beyond the leading order for the QED effects. It would therefore be desirable to be able to combine MBPT and the numerical QED approach in some systematic way, which seems to be necessary to achieve sufficient accuracy for light and medium-heavy elements. The present work represents one step in that direction.

The atomic fine-structure is entirely due to relativity and QED, with leading orders of $(Z\alpha)^2$ and $(Z\alpha)^3$, respectively, relative to the non-relativistic energies. For that reason the fine-structure is a good candidate for testing the theory, when very accurate experimental results are becoming available, particularly for heliumlike ions. For high Z a comparison between theory and experiment will test QED at strong electric fields and for low Z this can be used to determine the fine-structure constant, α, provided the theory of QED is trusted.

2 Time-independent perturbation theory. Quasi-degeneracy

In perturbation theory the Hamiltonian is normally partitioned into a zeroth-order Hamiltonian and a perturbation

$$H = H_0 + H'. \tag{1}$$

Working with a single reference or *model function*, Φ, the standard (Rayleigh-Schrödinger) perturbation theory gives the first-order contribution to the wave function

$$\Psi^{(1)} = \sum_{\Phi^i \neq \Phi} \frac{|\Phi^i\rangle\langle\Phi^i|H'|\Phi\rangle}{E_0 - E_0^i}. \tag{2}$$

The model function, Φ, is in this case an eigenfunction of H_0 and forms together with the remaining eigenfunctions the basis functions,

$$H_0\,\Phi = E_0\,\Phi \quad \text{and} \quad H_0\,\Phi^i = E_0^i\,\Phi^i.$$

This can easily be generalized to the case with several *degenerate* model functions, all of which are then excluded from the summation in (2).

In the case of *quasi-degeneracy* (very closely lying states), some of the energy denominators in (2) can be very small, which may cause serious *convergence problems*. In relativistic many-body perturbation theory, applied to the fine structure in the $1s2p$ multiplet of He-like systems,

the states $1s2p_{1/2}$ and $1s2p_{3/2}$ are very close in energy and hence strongly mixed for light elements. This has led to serious problems using a single model function [26], problems which can be remedied by using an *extended model space* [27,28,29].

We consider now a number of eigenfunctions of the Hamiltonian

$$H\,\Psi^\alpha = E^\alpha\,\Psi^\alpha \quad (\alpha = 1, 2, \cdots d), \tag{3}$$

referred to as the *target functions*. The relation between the target functions and the corresponding *model functions* is given by a *wave operator*,

$$\Psi^\alpha = \Omega\,\Psi_0^\alpha \qquad (\alpha = 1, 2 \cdots d). \tag{4}$$

In the *intermediate normalization* we apply here, the model functions are projections of the corresponding target functions on the model space,

$$\Psi_0^\alpha = P\,\Psi^\alpha \qquad (\alpha = 1, 2 \cdots d). \tag{5}$$

The wave operator satisfies the *Bloch equation* [27,30,28]

$$[\Omega, H_0]P = (H'\,\Omega - \Omega P H'\,\Omega)P. \tag{6}$$

Expanding the wave operator order by order, leads instead of (2) to the first-order contribution

$$\Omega^{(1)}|m\rangle = \sum_{i\in Q} \frac{|i\rangle\langle i|H'|m\rangle}{E_0^m - E_0^i}, \tag{7}$$

where m/i represent basis functions inside/outside the model space. The sum is here restricted to states in the complementary space (Q), outside the model space (P). The Bloch equation can also be used to derive the *linked-diagram expansion* for an extended model space, which can be expressed [27,28]

$$[\Omega, H_0]P = (H'\,\Omega - \Omega P H'\,\Omega)_{\rm Linked} P. \tag{8}$$

The last term represents what is known as *folded diagrams*.

In the general case the model functions are not eigenfunctions of H_0. Instead they are solutions of the secular equation

$$H_{\rm eff}\,\Psi_0^\alpha = E^\alpha\,\Psi_0^\alpha. \tag{9}$$

$H_{\rm eff}$ is matrix operator, acting in the model space and referred to as the *effective Hamiltonian*. *The eigenvectors of the effective Hamiltonian are the model functions* (4) *and the eigenvalues are the corresponding exact energies* (3). In intermediate normalization the effective Hamiltonian has the form

$$H_{\rm eff} = PH\Omega P = PH_0P + PH'\Omega P. \tag{10}$$

In the MBPT procedure with an extended model space, the states of the model space are excluded from the summations of the type (7), thus eliminating not only degenerate but also quasi-degenerate states. The contribution due to (quasi)degenerate states is included to all orders of perturbation theory by diagonalizing the effective Hamiltonian. This procedure has been shown to improve the convergence rate drastically in the case of quasi-degeneracy [29].

In the case of the $1s2p$ multiplet of heliumlike ions the two states $\left(s_{1/2}\,p_{1/2}\right)_{J=1}$ and $\left(s_{1/2}\,p_{3/2}\right)_{J=1}$ have the same symmetry, and for light elements they are closely spaced and hence strongly mixed.

By including these states in the model space their mixture will be appropriately taken care of, which might be quite difficult, using the standard procedure with single reference function.

The main question is now: **Can a similar procedure be applied in bound-state QED?** A major obstacle is here that the standard procedure for bound-state QED, the S-matrix formulation, requires *energy conservation* between the initial and final states and hence cannot be used to evaluate the elements of the effective Hamiltonian (9) *non-diagonal* in energy, needed to treat quasi-degeneracy using an extended model space. Therefore, the procedure has to be modified, as we shall demonstrate below.

3 Time-dependent perturbation theory

In order to find a procedure applicable also to a quasi-degenerate situation, we shall consider *time-dependent perturbation theory*, although the problems we shall study usually are time independent. The basic tool is here the *time-evolution operator*, U, which regulates the development of the wave function in time

$$\Psi(t) \propto U(t,t_0)\,\Psi(t_0) \qquad (t > t_0).$$

We work in the *interaction picture*, where the operators and wave functions are related to those in the conventional Schrödinger picture by [a]

$$O_{\rm I}(t) = \mathrm{e}^{\mathrm{i}H_0 t}\, O_{\rm S}\, \mathrm{e}^{-\mathrm{i}H_0 t}; \qquad \Psi_{\rm I}(t) = \mathrm{e}^{\mathrm{i}H_0 t}\, \Psi_{\rm S}(t).$$

In this picture the time-dependent Schrödinger equation takes the form

$$\mathrm{i}\frac{\partial}{\partial t}\Psi_{\rm I}(t) = H'_{\rm I}\,\Psi_{\rm I}(t),$$

which leads to the expansion [31]

$$U_\gamma(t,t_0) = 1 + \sum_{n=1}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_{t_0}^{t} \mathrm{d}t_n \int_{t_0}^{t} \mathrm{d}t_{n-1} \ldots \int_{t_0}^{t} \mathrm{d}t_1 T\big[H'_{\rm I}(t_n)\, H'_{\rm I}(t_{n-1}) \ldots H'_{\rm I}(t_1)\big] \mathrm{e}^{-\gamma(|t_1|+|t_2|\ldots+|t_n|)}, \quad (11)$$

where T is the time-ordering operator.

Due to the adiabatic damping, the perturbation vanishes in the limits $t \to \pm\infty$ and the exact wave function becomes equal to the unperturbed function in these limits, $\Phi = \Psi(\pm\infty)$. The wave function in time-independent theory corresponds to the time-dependent function at $t = 0$, $\Psi = \Psi(0)$.

Gell-Mann and Low [12] have shown that for a single reference function (closed-shell case), Φ, the function

$$\Psi(t) = \lim_{\gamma\to 0} \frac{U_\gamma(t,-\infty)\,\Phi}{\langle\Phi|U_\gamma(0,-\infty)|\Phi\rangle}$$

is a normalized eigenfunction of the Hamiltonian (provided the limit exists). The evolution operator has singularities due to *unlinked diagrams*, which are eliminated by the denominator.

When several reference or model functions are used (multi-dimensional model space), the Gell-Mann–Low procedure has to be modified [32,33],

$$\Psi^\alpha(t) = \lim_{\gamma\to 0} \frac{U_\gamma(t,-\infty)\,\phi^\alpha}{\langle\phi^\alpha|U_\gamma(0,-\infty)|\phi^\alpha\rangle}. \quad (12)$$

[a] We use here relativistic units: $c = m = \hbar = \epsilon_0 = 1$; $e^2 = 4\pi\alpha$.

ϕ^α are here certain 'parent' functions in the model space. In this case the evolution operator has singularities or quasi-singularities also for *linked* diagrams, when a model-space state appears as an intermediate state. This corresponds to the folded diagrams in time-independent MBPT, mentioned above.

In order to treat the (quasi)singularities, we rewrite the evolution operator, operating on the model space, as [25]

$$U(t,-\infty) = 1 + \widetilde{U}(t,-\infty)PU(0,-\infty), \tag{13}$$

leaving out the subscript γ. This leads to the expansion

$$\begin{aligned} U &= 1 + \widetilde{U} + \widetilde{U}P\widetilde{U} + \widetilde{U}P\widetilde{U}P\widetilde{U} + \cdots \\ \widetilde{U} &= U - 1 - \widetilde{U}P\widetilde{U} - \widetilde{U}P\widetilde{U}P\widetilde{U} - \cdots . \end{aligned} \tag{14}$$

$\widetilde{U}$ is referred to as the *reduced evolution operator* and can be shown to be *regular*, i.e., free from (quasi)singularities. The (quasi)singularities are eliminated by the *counterterms* ($-\widetilde{U}P\widetilde{U}$ etc.) in (14).

For $t = 0$ the definition (13) becomes

$$U(0,-\infty) = 1 + \widetilde{U}(0,-\infty)PU(0,-\infty),$$

which leads to

$$U(0,-\infty) = \big(1 + Q\,\widetilde{U}(0,-\infty)\big)PU(0,-\infty).$$

Inserted in the generalized Gell-Mann–Low relation (12) this gives

$$\Psi^\alpha = \Psi^\alpha(0) = \big[1 + Q\,\widetilde{U}(0,-\infty)\big]\,\Psi_0^\alpha,$$

where

$$\Psi_0^\alpha = P\Psi^\alpha = \frac{PU(0,-\infty)\,\phi^\alpha}{\langle\phi^\alpha|U(0,-\infty)|\phi^\alpha\rangle}.$$

This we can compare with the MBPT equation above (4), showing that the *wave operator* becomes

$$\boxed{\Omega = 1 + Q\,\widetilde{U}(0,-\infty).} \tag{15}$$

The effective interaction is defined

$$H'_{\rm eff} = H_{\rm eff} - PH_0P$$

and this can be expressed by means of the reduced evolution operator as [34,25]

$$\boxed{H'_{\rm eff} = P\Big[\mathrm{i}\frac{\partial}{\partial t}\widetilde{U}(t,-\infty)\Big]_{t=0}P.} \tag{16}$$

4 Bound-state QED

4.1 S-matrix

The S-matrix is related to the time-evolution operator by $S = U(\infty,-\infty)$. The S-matrix for single-photon exchange between electrons, represented by the Feynman diagram in Fig. 1, is given by

$$S^{(2)} = -\frac{1}{2}\iint \mathrm{d}^4x_1\,\mathrm{d}^4x_2\;\hat\psi^\dagger(x_1)\,\hat\psi^\dagger(x_2)\,\mathrm{i}I(x_2,x_1)\,\hat\psi(x_2)\,\hat\psi(x_1)\,\mathrm{e}^{-\gamma(|t_1|+|t_2|)}. \tag{17}$$

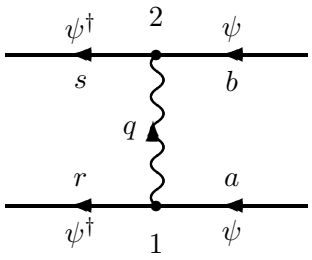

Figure 1: The S-matrix for single-photon exchange

Here [b],

$$\hat{\psi}(x) = c_j\,\phi_j(x); \qquad \hat{\psi}^\dagger(x) = c_j^\dagger\,\phi_j^\dagger(x) \tag{18}$$

are the electron-field operators in the *interaction picture*, γ is an *adiabatic-damping factor*, which eventually goes to zero, $\gamma \to +0$, and

$$I(x_2, x_1) = e^2 \alpha_1^\mu \alpha_2^\nu\, D_{F\mu\nu}(x_2, x_1) \tag{19}$$

represents the electron-electron interaction, $D_{F\mu\nu}(x_2, x_1)$ being the *photon propagator*. Identification with the second-quantized expression,

$$S^{(2)} = \frac{1}{2}\, c_i^\dagger c_j^\dagger \left\langle ij\middle|S^{(2)}\middle|kl\right\rangle c_l c_k, \tag{20}$$

yields the 'matrix element'

$$\begin{aligned}\left\langle rs\middle|S^{(2)}(x_1,x_2)\middle|ab\right\rangle &= -\iint \mathrm{d}^4x_1\,\mathrm{d}^4x_2\;\phi_r^\dagger(x_1)\phi_s^\dagger(x_2)\,\mathrm{i}I(x_2,x_1)\,\phi_a(x_1)\,\phi_b(x_2)\,\mathrm{e}^{-\gamma(|t_1|+|t_2|)} \\ &= -\mathrm{i}\iint \mathrm{d}t_1\,\mathrm{d}t_2\int\frac{\mathrm{d}z}{2\pi}\left\langle rs\middle|I(z)\middle|ab\right\rangle \mathrm{e}^{-\mathrm{i}t_1(q-z)}\,\mathrm{e}^{-\mathrm{i}t_2(q'+z)}\,\mathrm{e}^{-\gamma(|t_1|+|t_2|)},\end{aligned} \tag{21}$$

where $I(z)$ is the Fourier transform of (19) and $q = \varepsilon_a - \varepsilon_r$; $q' = \varepsilon_b - \varepsilon_s$. After integrations over time and z this becomes

$$\left\langle rs\middle|S^{(2)}\middle|ab\right\rangle = -2\pi\Delta_\gamma(q+q')\left\langle rs\middle|I(q)\middle|ab\right\rangle,$$

where

$$\int_{-\infty}^{\infty}\mathrm{d}t\,\mathrm{e}^{-\mathrm{i}ty-\gamma|t|} = \frac{2\gamma}{y^2+\gamma^2} = 2\pi\,\Delta_\gamma(y). \tag{22}$$

The relation between the S-matrix and the energy shift is given by the Sucher formula [13,31]

$$\Delta E = \lim_{\gamma\to 0}\frac{\mathrm{i}\gamma}{2}\,\frac{\sum_n n\langle rs|S^{(n)}|ab\rangle}{\langle rs|S|ab\rangle}, \tag{23}$$

[b] We use here the *Furry picture*, where the single-electron orbitals are solutions of the Dirac equation in the field of the nucleus (and possibly other electrons), $V(r)$,

$$h_D\,\phi_j = \left[\mathbf{p}\cdot\boldsymbol{\alpha} + \beta + V(r)\right]\phi_j = \varepsilon_j\,\phi_j.$$

$c_j^\dagger/c_j$ are the corresponding creation/annihilation operators. We apply the summation convention with summation over repeated indices.

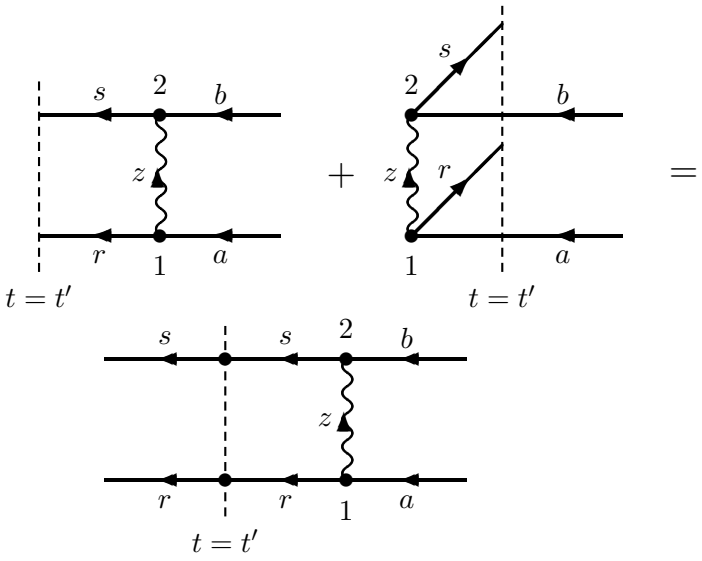

Figure 2: The covariant evolution operator for single-photon exchange.

which in the lowest order ($n = 2$) becomes

$$\Delta E = \lim_{\gamma\to 0} \mathrm{i}\gamma \langle rs|S^{(2)}|ab\rangle. \tag{24}$$

In the present case this gives

$$\Delta E = \delta_{q,-q'} \left\langle rs\middle|V_{\mathrm{eq}}(q)\middle|ab\right\rangle. \tag{25}$$

The Kronecker delta factor implies here that the result is nonvanishing only for $q + q' = 0$ or $\varepsilon_a + \varepsilon_b = \varepsilon_r + \varepsilon_s$, which means that energy must be conserved between the initial and final states. This makes the method inapplicable for treating quasi-degeneracy, using the method of extended model space.

4.2 Covariant form of the evolution operator

We shall now demonstrate how the evolution operator, discussed in Sec. 3, can be used to treat quasi-degeneracies also in QED problems. In this case, however, it is necessary to allow time to run also in the *backward* direction in order to include the contribution from positron states. Therefore, we have to generalize the standard procedure, as illustrated for single-photon exchange in Fig. 2. This corresponds to the expression [24,25]

$$\begin{aligned} U^{(2)}_{\mathrm{Cov}}(t', -\infty) = -\frac{1}{2} \iint \mathrm{d}^4x_1\, \mathrm{d}^4x_2 \, \Big[\Theta(t' - t_1)\, \hat\psi^\dagger_+(x_1) - \Theta(t_1 - t')\, \hat\psi^\dagger_-(x_1)\Big] \times \\ \times \Big[\Theta(t' - t_2)\, \hat\psi^\dagger_+(x_2) - \Theta(t_2 - t')\, \hat\psi^\dagger_-(x_2)\Big]\, \mathrm{i}I(x_2, x_1)\, \hat\psi(x_2)\, \hat\psi(x_1)\, \mathrm{e}^{-\gamma(|t_1|+|t_2|)}, \end{aligned} \tag{26}$$

where Θ is the Heaviside step function. The time integrations are here performed over *all* times, making this operator *covariant* – like the S operator but in contrast to the evolution operator for forward evolution only (11). The operator (26) can also be expressed by means of the *electron propagator* as

$$\begin{aligned} U^{(2)}_{\mathrm{Cov}}(t', -\infty) \, = -\frac{1}{2} \iint \mathrm{d}^3x'_1\, \mathrm{d}^3x'_2\, \hat\psi^\dagger(x'_1)\, \hat\psi^\dagger(x'_2) \, \times \\ \times \iint \mathrm{d}^4x_1\, \mathrm{d}^4x_2\, \mathrm{i}S_F(x'_2, x_2)\, \mathrm{i}S_F(x'_1, x_1)\, \mathrm{i}I(x_2, x_1)\, \hat\psi(x_2)\, \hat\psi(x_1)\, \mathrm{e}^{-\gamma(|t_1|+|t_2|)}, \end{aligned} \tag{27}$$

which yields the matrix element

$$\langle rs\big|U^{(2)}_{\rm Cov}(t',-\infty)\big|ab\rangle = -\iint {\rm d}^3x_1'\,{\rm d}^3x_2'\,\phi_r^\dagger(x_1')\phi_s^\dagger(x_2')\,\times$$
$$\times\iint {\rm d}^4x_1\,{\rm d}^4x_2\,{\rm i}S_F(x_1',x_1)\,{\rm i}S_F(x_2',x_2)\,{\rm i}I(x_2,x_1)\,\phi_a(x_1)\,\phi_b(x_2)\,{\rm e}^{-\gamma(|t_1|+|t_2|)} =$$
$$=\iint {\rm d}t_1\,{\rm d}t_2\,\Big\langle rs\Big|S_F(x_1',x_1)\,S_F(x_2',x_2)\,{\rm i}I(x_2,x_1)\,\Big|ab\Big\rangle\,{\rm e}^{{\rm i}t'(\varepsilon_r+\varepsilon_s)}\,{\rm e}^{-{\rm i}t_1\varepsilon_a-{\rm i}t_2\varepsilon_b}\,{\rm e}^{-\gamma(|t_1|+|t_2|)}. \quad (28)$$

After time integrations this becomes

$$\Big\langle rs\,\Big|U^{(2)}_{\rm Cov}(t',-\infty)\Big|\,ab\Big\rangle = \langle rs\,\big|V(q,q')\big|\,ab\rangle\,\frac{{\rm e}^{-{\rm i}t'(q+q'+{\rm i}\gamma_r+{\rm i}\gamma_s)}}{q+q'+{\rm i}\gamma_r+{\rm i}\gamma_s}, \quad (29)$$

where γ_x has the same sign as ε_x. Using the Feynman gauge we obtain

$$V(q,q') = \int {\rm d}k\,f(k)\Big[\frac{1}{q-(k-{\rm i}\gamma)_r}+\frac{1}{q'-(k-{\rm i}\gamma)_s}\Big] \quad (30)$$
$$f(k) = -\frac{e^2}{4\pi^2\,r_{12}}\,(1-\boldsymbol{\alpha}_1\cdot\boldsymbol{\alpha}_2)\,\sin(kr_{12}).$$

The contributions to the first-order wave operator (15) and effective interaction (16) then become

$$\Omega^{(1)} = Q\,U^{(2)}_{\rm Cov}(0,-\infty) = \sum_{|rs\rangle\in Q}\frac{|rs\rangle\langle rs|V(q,q')|ab\rangle}{\varepsilon_a+\varepsilon_b-\varepsilon_r-\varepsilon_s} \quad (31)$$

$$\langle rs\big|H^{'(1)}_{\rm eff}\big|ab\rangle = \Big\langle rs\Big|\Big[{\rm i}\frac{\partial}{\partial t}U^{(2)}_{\rm Cov}(t,-\infty)\Big]_{t=0}\Big|ab\Big\rangle = \langle rs\big|V(q,q')|ab\rangle \quad (|rs\rangle\in P). \quad (32)$$

In the first case the state $|rs\rangle$ lies in the complementary space (Q) (outside the model space, P) and in the second case inside the model space. The effective interaction agrees with the S-matrix result, when the initial and final energies are the same. But the important point is here that the evolution-operator result is valid also when these energies are different, making the procedure applicable also to an extended model space with several unperturbed energies.

Another important advantage of the evolution-operator method is that – in contrast to the S-matrix formulation (23) – no limiting procedure of the adiabatic damping factor γ is needed. (This factor is here needed only to indicate the position of possible poles.) This implies that the integrations can be performed independently with *exact energy conservation* at each vertex. This simplifies considerably the treatment of (quasi)singularities, as we shall demonstrate with the two-photon exchange below.

4.3 Two-photon exchange

There are two Feynman diagrams representing the two-photon exchange between the electrons, the 'ladder diagram' and the 'crossed-photon diagram', illustrated in Fig. 3. The covariant evolution operator for the ladder diagram is given by

$$\Big\langle rs\,\Big|U^{(4)}_{\rm Cov}(t',-\infty)\Big|\,ab\Big\rangle = \Big\langle rs\Big|\iint {\rm d}^4x_3\,{\rm d}^4x_4\,{\rm i}S_F(x_3',x_3)\,{\rm i}S_F(x_4',x_4)\,{\rm i}I(x_4,x_3)\;\times$$
$$\times\iint {\rm d}t_1\,{\rm d}t_2\,{\rm i}S_F(x_3,x_1)\,{\rm i}S_F(x_4,x_2)\,{\rm i}I(x_2,x_1)\big|ab\big\rangle\,{\rm e}^{{\rm i}t'(\varepsilon_r+\varepsilon_s)}\,{\rm e}^{-{\rm i}t_1\varepsilon_a-{\rm i}t_2\varepsilon_b}\,{\rm e}^{-\gamma(|t_1|+|t_2|+|t_3|+|t_4|)}, \quad (33)$$

and similarly for the crossed diagram.

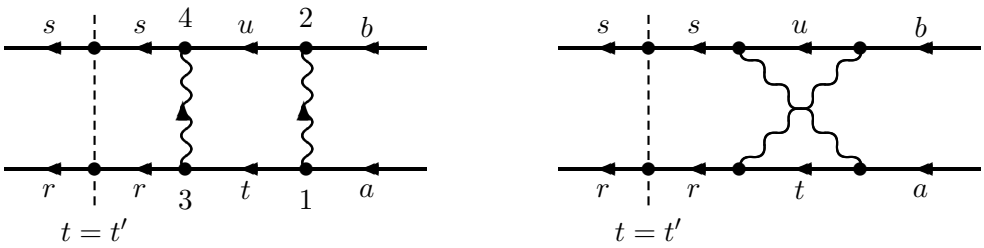

Figure 3: Two-photon exchange diagrams, the ladder diagram (left) and the crossed-photon diagram (right).

The ladder diagram has a (quasi)singularity, when the intermediate state (tu) is (quasi)-degenerate with the initial state (ab). In order to study this (quasi)singularity, we first separate the ladder into a *separable* and a *non-separable* part. A diagram is said to be *separable*, if *the two photons do not overlap in time*, or in other words that there exists an intermediate time $(t = t'')$, for which there is no free photon, as indicated in the leftmost diagram in Fig. 4. *If the intermediate state of a separable diagram lies in the model space, the diagram is said to be reducible.*

It can be shown that the separable two-photon diagram is given by [25]

$$\left\langle rs \left| U^{(4)}_{\rm Sep}(t',-\infty) \right| ab \right\rangle = \left\langle rs \middle| V(q+p',q'+p) \middle| tu \right\rangle \left\langle tu \middle| V(p,p') \middle| ab \right\rangle \frac{\mathrm{e}^{-\mathrm{i}t'(q+q')}}{(q+q')(p+p')}, \tag{34}$$

where $q = \varepsilon_a - \varepsilon_r$; $q' = \varepsilon_b - \varepsilon_s$; $p = \varepsilon_a - \varepsilon_t$; $p' = \varepsilon_b - \varepsilon_u$ and $V(q,q')$ is given by (30). The corresponding contribution to the effective Hamiltonian is then, using (16),

$$\frac{\langle rs\,|V(q+p',q'+p)|\,tu\rangle\ \langle tu\,|V(p,p')|\,ab\rangle}{p+p'}, \tag{35}$$

which is (quasi)singular, when the intermediate state (tu) is (quasi)degenerate with the initial state (ab) $(p+p' \approx 0)$.

In the expression for the effective interaction (16), the *reduced* evolution operator (11) appears, which in the present case is given by

$$\widetilde{U}^{(4)} = U^{(4)} - U^{(2)}PU^{(2)}. \tag{36}$$

The *counterterm*, $-U^{(2)}PU^{(2)}$, is here

$$\frac{\langle rs\,|V(q-p,q'-p')|\,tu\rangle\ \langle tu\,|V(p,p')|\,ab\rangle}{p+p'}. \tag{37}$$

If we introduce $W(E_0) = V(q+p',q'+p) = V(E_0-\varepsilon_r-\varepsilon_u, E_0-\varepsilon_s-\varepsilon_t)$ with $\Delta E = p+p' = E_0-\varepsilon_t-\varepsilon_u$, the contribution to the effective Hamiltonian can be expressed

$$\frac{\langle rs\,|W(E_0)-W(E_0-\Delta E)|\,tu\rangle}{\Delta E}\ \left\langle tu \left| V(p,p') \right| ab \right\rangle. \tag{38}$$

This expression is *regular* – free from (quasi)singularities. When $\Delta E \to 0$, the result becomes

$$\left\langle rs \middle| \Big[\frac{\delta}{\delta E} W(E)\Big]_{E=E_0} \middle| tu \right\rangle \langle tu | V(p,p') | ab \rangle, \tag{39}$$

which identical to the S-matrix result. The result (38), however, is more general and (as the single-photon result) valid for a model space that is not necessarily degenerate. A similar result can be derived for the wave operator, which is also regular.

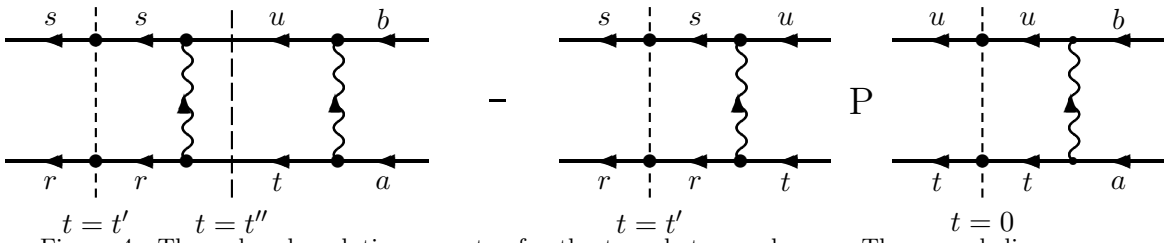

Figure 4: The reduced evolution operator for the two-photon exchange. The second diagram represents the counterterm $U^{(2)}PU^{(2)}$ in (36)

When a separable two-photon diagram is *irreducible* (not reducible), then there is no counterterm, and the contribution to the effective Hamiltonian is given by (35). The summation is then performed only over intermediate states in the *complementary space* (Q), and there is no (quasi)degeneracy. This is then quite similar to the standard expression of second-order perturbation theory (2), which is entirely contained in the separable two-photon diagram. In addition, the separable two-photon diagram contains QED effects – beyond standard MBPT – due to negative energy states and retardation.

The remaining, non-separable part of the ladder diagram is always regular, and this is also the case of the crossed two-photon diagram, which has no reducible part. These parts can be evaluated in a straightforward manner. The non-separable diagrams represent pure QED effects – with no analogy in MBPT.

The above illustrates the close analogy between standard MBPT and bound-state QED using the covariant-evolution-operator method – a fact which may open up possibilities of combining QED and MBPT in a more systematic fasion than has previously been possible.

5 Results and discussion

We have applied the covariant-evolution-operator method to evaluate the fine-structure separation of the $1s2p$ multiplet of the He-like ions of Ne and Ar, and the results are reproduced in Table 2. Our calculations include the exchange of one and two photons between the electrons, as described above, which contains relativistic many-body effects to second order in addition to the QED effects. Furthermore, we have included relativistic electron correlation effects *beyond* second order from a separate many-body calculation. The remaining QED efects, not included in the diagrams evaluated, namely the self-energy and vacuum-polarization contributions, are estimated by means of the analytical $Z\alpha$ expansion. Our numerical results are compared with those of Drake [35] and Plante *et al.* [26], as well as with available experimental results [11,9].

Our calculation represents the first application of bound-state QED to a quasi-degenerate fine-structure separation, using a numerical technique to *all orders of* $Z\alpha$. The results of our calculations agree very well with available experimental data.

Our results agree also well with those of Drake and Plante *et al.* The calculations of Drake are performed using highly correlated non-relativistic wave functions of Hylleraas type with relativistic and QED effects estimated from the analytical expansion. In the work of Plante *et al.* a relativistic MBPT procedure is used, with the QED correction separately added.

For the elements presented here the difference between the theoretical results is hardly significant compared to the experimental and theoretical uncertainties. (For the argon ion the result of Drake differs from the experimental result by 2-3 standard deviations, which is likely due to inaccuracy in the relativistic correction.) When higher accuracy is needed, however,

Table 2: Comparison between experiment and theory for the fine-structure separations the $1s2p$ multiplet of some He-like ions (in μ Hartree $\approx 27{,}2$ μ eV).

Z	$^3P_1 - {}^3P_0$	$^3P_2 - {}^3P_0$	$^3P_2 - {}^3P_1$
10	**1371(7)**	**8458(2)**	Expt'l [9]
	1361(6)	8455(6)	Drake [35]
	1370	8469	Plante *et al.* [26]
	1373	8464	Present [25]
18		**124960(30)**	Expt'l [11]
	23600(60)	124810(60)	Drake [35]
	23690	124942	Plante *et al.* [26]
	23792	124938	Present [25]

higher-order QED effects will be important. Already for argon we have found that the effects beyond the leading $(Z\alpha)^3$ order are at least comparable to that of the leading term.

As can be seen from Table 1, quite accurate experimental data are available for neutral helium as well as for the ions of lithium and fluorine. For very low Z the numerical problems increase, due to slow convergence of the partial-wave expansion. In addition, the electron correlation plays here a relatively more important role, and two-photon exchange may not be sufficient. For these reasons, it will be difficult at present to compete with the analytical results for He and Li^+. In order to achieve higher accuracy with the numerical technique, it would be necessary to combine the QED and MBPT procedures in some way, and developments along these lines are in progress at our laboratory. A good test of the present procedure described here, however, would be to try to reproduce the experimental result of the fluorine ion, which has an accuracy of the order of one ppm. Here high-order QED effects will certainly be significant. Such an accurate numerical result could then be used to test the analytical expansion and possible to estimate higher-order non-calculated terms of that expansion. In this way the numerical results could contribute to the accuracy of the theoretical result also for very low Z and possibly to the evaluation of the fine-structure constant.

Acknowledgments

This work has been supported by the Swedish Natural Science Research Council and the Alexander von Humboldt Foundation.

References

1. F. Minardi, G. Bianchini, P. C. Pastor, G. Guisfredi, F. S. Pavone, and M. Inguscio. *Phys. Rev. Lett.*, 82:1112, 1999.
2. C. H. Storry, M. C. George, and E. A. Hessels. *Phys. Rev. Lett.*, 84:3274, 2000.
3. J. Castillega, D. Livingston, A. Sanders, and D. Shiner. *Phys. Rev. Lett.*, 84:4321, 2000.
4. K. Pachucki and J. Sapirstein. *J. Phys. B*, 33:5297, 2000.
5. M. C. George, L. D. Lombardi, and E. A. Hessels. *Phys. Rev. Lett.*, 87:173002, 2001.
6. E. Riis, A. G. Sinclair, O. Poulsen, G. W. F. Drake, W. R. C. Rowley, and A. P. Levick. *Phys. Rev. A*, 49:207, 1994.
7. J. K. Thompson, D. J. H. Howie, and E. G. Myers. *Phys. Rev. A*, 57:180, 1998.
8. E. G. Myers, H. S. Margolis, J. K. Thompson, M. A. Farmer, J. D. Silver, and M. R. Tarbutt. *Phys. Rev. Lett.*, 82:4200, 1999.
9. W. Curdt, E. Landi, K. Wilhelm, and U. Feldman. *Phys. Rev. A*, 62:022502, 2000.

10. E. G. Myers and M. R. Tarbutt. *Phys. Rev. A*, 61:010501R, 1999.
11. K. W. Kukla, A. E. Livingston, J. Suleiman, H. G. Berry, R. W. Dunford, D. S. Gemmel, E. P. Kantor, S. Cheng, and L. J. Curtis. *Phys. Rev. A*, 51:1905, 1995.
12. M. Gell-Mann and F. Low. *Phys. Rev.*, 84:350, 1951.
13. J. Sucher. *Phys. Rev.*, 107:1448, 1957.
14. S. Blundell, P. J. Mohr, W. R. Johnson, and J. Sapirstein. *Phys. Rev. A*, 48:2615, 1993.
15. I. Lindgren, H. Persson, S. Salomonson, and L. Labzowsky. *Phys. Rev. A*, 51:1167, 1995.
16. H. Persson, S. Salomonson, P. Sunnergren, and I. Lindgren. *Phys. Rev. Lett.*, 76:204, 1996.
17. V. A. Yerokhin, A. N. Artemyev, V. M. Shabaev, and G. Soff. *Phys. Lett. A*, 234:361, 1997.
18. P. J. Mohr and J. Sapirstein. *Phys. Rev. A*, 62:052501, 2000.
19. B. Åsén, S. Salomonson, and I. Lindgren. *Phys. Rev. A*, accepted, 2002.
20. V. M. Shabaev. *J. Phys. B*, 26:4703, 1993.
21. V. M. Shabaev. *Phys. Rev. A*, 50:4521, 1994.
22. V. M. Shabaev and I. G. Fokeeva. *Phys. Rev. A*, 49:4489, 1994.
23. V. A. Yerokhin, A. N. Artemyev, T. Beier, G. Plunien, V. M. Shabaev, and G. Soff. *Phys. Rev. A*, 60:3522, 1999.
24. I. Lindgren. *Mol. Phys.*, 98:1159, 2000.
25. I. Lindgren, B. Åsén, S. Salomonson, and A.-M. Mårtensson-Pendrill. *Phys. Rev. A*, 64:062505, 2001.
26. D. R. Plante, W. R. Johnson, and J. Sapirstein. *Phys. Rev. A*, 49:3519, 1994.
27. I. Lindgren. *J. Phys. B*, 7:2441, 1974.
28. I. Lindgren and J. Morrison. *Atomic Many-Body Theory.* Springer-Verlag, Berlin, 1986.
29. A.-M. Mårtensson-Pendrill, I. Lindgren, E. Lindroth, S. Salomonson, and D. S. Staudte. *Phys. Rev. A*, 51:3630, 1995.
30. V. Kvasnička. *Adv. Chem. Phys.*, 36:345, 1977.
31. S. S. Schweber. *An Introduction to Relativistic Quantum Field Theory.* Harper and Row, N.Y., 1961.
32. T. T. S. Kuo, S. Y. Lee, and K. F. Ratcliff. *Nucl. Phys. A*, 176:65, 1971.
33. G. Oberlechner, F. Owono-N'-Guema, and J. Richert. *Nouvo Cimento B*, 68:23, 1970.
34. R. W. Jones and F. Mohling. *Nucl. Phys. A*, 151:420, 1970.
35. G. Drake. *Can. J. Phys.*, 66:586, 1988.